



Department of Pesticide Regulation



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MEMORANDUM

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TO: Sue Edmiston, Agriculture Program Supervisor III
Worker Health and Safety Branch **HSM-05003**

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SUBJECT: CHLORPYRIFOS FIELD SPIKE DEGRADATION STUDY, PROJECT #0403

Background

In 2003, the Worker Health and Safety Branch, Exposure Monitoring Program (EMP) conducted exposure monitoring of two irrigators potentially exposed to chlorpyrifos. Field fortification and blanks of each sample matrix accompanied exposure-monitoring samples for each worker monitored. Initial results from those fortifications and blanks showed fairly low recovery and some contamination of the blanks. Recoveries from the handwash and face/neck wipes were especially worrisome (10-20%). The method validation demonstrated good recoveries from laboratory fortified sample matrix. The analytical laboratory conducted a storage stability study focusing on temperature, time and solution concentration. The storage stability recoveries were reasonable and did not duplicate or confirm the low recoveries found in the field spikes.

The Project 0301 study objective was to evaluate recovery of chlorpyrifos from field fortification on dermal matrices used in project 0301 (Exposure of Cotton Irrigators to Pesticides in Sprinkler and Furrow Irrigation Systems). With this project we planned to evaluate the effects of temperature and sun on the field fortification of clothing samples and the effects of plastic storage containers and freezing on the handwash and face/neck wipe samples.

Methods

1. The project plan called for fortifying the same matrices used in Project 0301 under hot, sunny environmental conditions to mimic expected field conditions.
2. Field fortification samples and blanks were prepared in open space at the California Department of Food and Agriculture Center for Analytical Chemistry (CDFA/CAC) parking lot and fortification and sample storage/pickup was completed in one day.
3. CDFA/CAC provided 20 µg, 200 µg and 1 mg chlorpyrifos solutions and performed the sample fortification.
4. EMP provided the t-shirts and assisted in setting up test materials, labeling and study documentation.
5. *Sample Fortification, Collection and Extraction:* Table 1 shows the fortification matrix for this project.

T-Shirts - Cotton (100%) t-shirts (2 replicates at each fortification level and each sampling interval) were fortified at 20 µg, 200 µg and 1 mg. The blank t-shirts and those fortified at



20 and 200 µg were left out in the sun (to mimic San Joaquin Valley temperatures) for 0, 2, 4, 6, and 7 hours. T-shirts fortified at 1 mg were collected at 0, 4 and 7 hours. All t-shirt samples collected up to 6 hours post-fortification were extracted the same day. Samples removed from the sun exposure at 7 hours were placed in the refrigerator and extracted the next day.

Handwashes – All handwash samples were fortified at 20 µg. One set (2 replicates) was placed in glass containers and extracted immediately. Handwash samples (one set of 2 replicates in glass and one set of two replicates in plastic) were placed in the freezer (to mimic field storage on dry ice). All frozen samples were analyzed 72 hours after fortification, allowing time for thawing. A fourth set of handwash samples in glass was placed in the refrigerator (to mimic field storage on ice) and extracted at 7 hours. Another set of handwash samples (2 replicates) in glass containers was placed at room temperature to mimic samples not exposed to direct sunlight and extracted at 8 hours.

Face/neck Wipes – All face/neck wipes were fortified at 20 µg. Two sets (2 replicates each set) were stored in the freezer (to mimic field storage on dry ice) and two sets in a refrigerator (to mimic storage on ice). One set under each storage condition type was immediately collected and extracted. One set stored in the refrigerator was collected and extracted at 8 hours post-fortification. The final set of replicates, stored frozen, was removed from frozen storage 2 days post-fortification, allowed to thaw for a day and then extracted.

Table 1: Fortification matrix and sampling intervals

Matrix	Fortification	No. of samples collected various intervals					
		0 hrs	2 hrs	4 hrs	6 hrs	7 hrs	8 hrs
T-shirt	Blank	2				2	
T-shirt	20 µg	2	2	2	2	2	
T-shirt	200 µg	2	2	2	2	2	
T-shirt	1 mg	2		2		2	
Handwash in glass (frozen)	20 µg	NS ^a					^b
Handwash in plastic (frozen)	20 µg	NS ^a					^b
Handwash in glass (refrigerated)	20 µg	NS ^a					2
Handwash in glass (room temp.)	20 µg	2					2
Face/neck wipe (frozen)	20 µg	2					^b
Face/neck wipe (refrigerated)	20 µg	2					2

^a No sample (NS)

^b Frozen samples placed in freezer immediately after fortification; they were removed 2 days later and allowed to thaw a day before extraction.

6. EMP placed a temperature logger outside with the t-shirt samples to record the temperatures during the course of the study.
7. T-shirt and face/neck wipe samples were extracted with ethyl acetate according to analytical method WHS-SM-3_Clothing. Handwash samples were extracted with ethyl acetate according to analytical method WHS-SM-2_Handwash. All extracts were analyzed on and Hewlett-Packard 5890 GC/FPD.

Results

Temperature was measured using an Onset Stowaway[®] XTI Internal/External Temperature Logger. Temperatures on the study day were 69° F when the samples were set outside and 101 °F when the samples were collected because of loss of direct sunlight exposure. Figure 1 shows the temperature range over the course of the study period. This corresponds reasonably well with the temperatures experienced during the two days of irrigator exposure monitoring where the maximum temperature was 96° and 105 °F.

Figure 1. Temperature range (°F) over the course of the study period, April 27, 2004

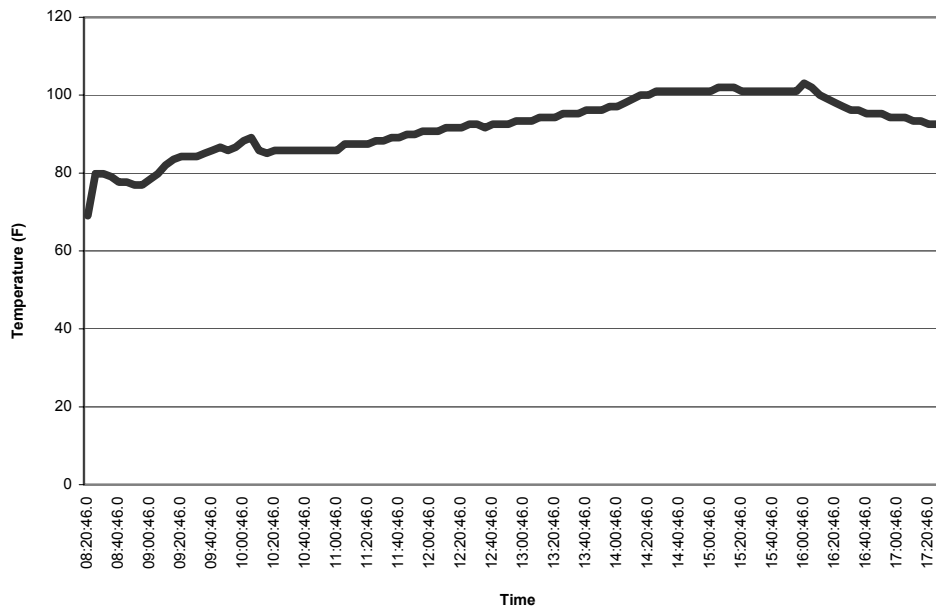


Table 2 shows that the concentration of chlorpyrifos on the T-shirts decreased at approximately the same rate for all fortification levels ranging from a zero-hour value of approximately 90% to a low around 60% at 7 hours. As temperature increases, chlorpyrifos quickly dissipates to recoveries that are below acceptable ranges (70-120%).

Table 2: T-Shirt fortification sample results

Fortification Level (µg)	Sample Collection Time (hours)	Replicate	Chlorpyrifos (µg/sample)	Recovery (%)	
				Sample data	Average
1000 (fortification completed at 11:15 AM)					
	0	A	907	90.7	91
	0	B	912	91.2	
	4	A	690	69.0	69.3
	4	B	695	69.5	
	7	A	664	66.4	66.9
	7	B	674	67.4	
200 (fortification completed at 11:30 AM)					
	0	A	177	88.5	90
	0	B	183	91.5	
	2	A	152	76.0	75.8
	2	B	151	75.5	
	4	A	130	65.0	69.5
	4	B	148	74.0	
	6	A	133	66.5	66.3
	6	B	132	66.0	
	7	A	110	55.0	60
	7	B	130	65.0	
20 (fortification completed at 12:00 PM)					
	0	A	17.1	85.5	84.3
	0	B	16.8	83.0	
	2	A	15.2	76.0	76.8
	2	B	15.5	77.5	
	4	A	13.2	66.0	65
	4	B	12.8	63.9	
	6	A	12.0	59.8	61.2
	6	B	12.5	62.6	
	7	A	11.1	55.6	59.3
	7	B	12.6	63.2	
	7	C ^a	11.8	59.0	
^a – A third sample was run for this replicate to check if values were still within the recovery range.					

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The results of the handwash samples (Table 3) indicate that glass storage is probably superior to plastic. However, the recoveries for both storage containers were inconsistent and below acceptable levels (70-120%). There was no noticeable difference between percent recovery of samples stored in glass containers frozen, refrigerated or at room temperature. However, plastic containers are a poor candidate for sample storage as demonstrated by the low percent recovery.

Table 3: Handwash fortification sample results

Fortification Level (µg)	Sample Storage	Sample Collection (hours)	Replicate	Chlorpyrifos (µg/sample)	Percent Recovery	
					Sample Data	Average
20	Glass/Frozen	0	A	9.11	45.6	57.2
		0	B	13.73	68.7	
		8	A	12.92	64.6	66.8
		8	B	13.77	68.9	
20	Plastic/Frozen	0	A	4.26	21.3	21.9
		0	B	4.49	22.5	
		8	A	2.39	12.0	10.9
		8	B	1.95	9.75	
20	Glass/Refrigerated	0	A	no sample ^a		-
		0	B	no sample		
		8	A	13.59	68.0	70.1
		8	B	14.43	72.1	
<u>20</u>	Glass/Room Temperature	72	A	10.1	50.5	61.3
		72	B	14.42	72.1	

^a –No samples were taken for “0” hours because the number of samples needed were miscounted the samples.

Whether frozen or refrigerated the recoveries for the face/neck wipes were no greater than 35% (Table 4). These recoveries are unacceptable. Table 5 presents the laboratory quality control samples. Recoveries for laboratory fortification were all within acceptable ranges.

Table 4: Neck/facewipe fortification sample results

Fortification Level (µg)	Sample Storage	Sample Collection (hours)	Replicate	Chlorpyrifos (µg/sample)	Percent Recovery	
					Sample Data	Average
20	Frozen	0	A	7.18	35.9	33.6
		0	B	6.25	31.3	
		8	A	6.65	33.3	29.2
		8	B	5.02	25.1	
	Refrigerated	0	A	4.92	24.6	26.9
		0	B	5.84	29.2	
		8	A	5.68	28.4	27
		8	B	5.09	25.5	

Table 5: Laboratory quality control sample results

Sample Matrix	Sample Type	Replicate	Results (µg/sample)	Recovery (%)
T-Shirt				
	Reagent blank		0.5 µg/sample	
	Matrix blank	0 hour sample collection	1.18 µg/sample ^a	
	Matrix blank	7 hour collection	0.82 µg/sample ^a	
Handwash				
	Matrix blank		ND	
	Matrix spike		18.2	90.9
Face/neck				
	Foil backing		0.37µg/sample	
	Matrix blank		0.13 µg/sample	
Field spike solution ^b				
		SF 0007A	17.66 µg/µL	88.3
		SF 0007B	17.86 µg/µL	89.3
		SF 0008	19.35 µg/µL	96.8
^a Positive T-shirt blanks are possibly due to limited auto sampler wash volume. This was considered a minor problem and didn't change the evaporation curve. ^b Lab spike solution (always refrigerated)				

Conclusion

The temperature peaked at approximately 101°F during the study. The concentration of chlorpyrifos on the t-shirt sample matrix seems to decrease at a high rate under high temperature conditions. This study does not answer the questions of degradation vs. volatilization. Chlorpyrifos does not appear to be stable under the study conditions, yielding less than ideal results and is an inappropriate active ingredient for using on a study where high temperature is a factor.